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THE REDUCTION OF SULFURYL CHLORIDE AT TEFLON-BONDED CARBON CATH--ETC(U)  
JAN 81 S GILMAN, W WADE

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THE REDUCTION OF SULFURYL CHLORIDE AT TEFLON-BONDED CARBON  
CATHODES



S. GILMAN  
W. WADE, JR.

ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

JANUARY 1981

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Polarization and discharge curves were measured for sulfuryl chloride reduction at Teflon-bonded carbon cathodes fabricated using a number of different carbon powders. Lithium chloroaluminate was utilized as electrolyte solute. At moderate current densities, cathode polarization tends to normalize with respect to Brunauer, Emmett, Teller (B.E.T.) surface area of the carbon. Cathode life increases with increased porosity of the electrode. The porosity is required for good accommodation of product LiCl. A formulation incorporating both high B.E.T. area and porosity was developed and found to provide good |                                   |   |  |

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## 10. ABSTRACT - Continued.

electrochemical performance against lithium counter-electrodes.

When sulfuryl chloride is reduced at the optimized cathode (against a lithium anode), the main products of reaction are LiCl (which is quantitatively deposited within the electrode's pores) and SO<sub>2</sub>. [This suggests the overall cell reaction: 2 Li+SO<sub>2</sub>Cl<sub>2</sub> → 2 LiCl+SO<sub>2</sub>. The addition of Cl<sub>2</sub> or SO<sub>2</sub> to the electrolyte causes decrease or increase of cathode polarization, respectively. This may be taken as evidence that the reduction, at moderate current densities, occurs through a Cl<sub>2</sub> intermediate resulting from heterogeneous decomposition of SO<sub>2</sub>Cl<sub>2</sub>. Reduction of undissociated SO<sub>2</sub>Cl<sub>2</sub> may occur at high current densities or after the active area of the electrode is significantly reduced through deposition of product LiCl.]

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# THE REDUCTION OF SULFURYL CHLORIDE AT TEFLON-BONDED CARBON CATHODES

## INTRODUCTION

The potential usefulness of sulfuryl chloride for lithium inorganic electrolyte cells was recognized a number of years ago.<sup>1-3</sup> However, development of a practical lithium-sulfuryl chloride cell has generally been assigned lower priority, by both Governmental and industrial organizations, than the corresponding lithium-thionyl chloride system. One reason for the relative inattention to sulfuryl chloride cell technology has been the observed dissipation of the apparent high voltage and capacity advantage (observed at low current densities) when experimental cells utilizing Teflon-bonded carbon (Shawinigan black) cathodes are discharged at high rates.<sup>4</sup> It was the purpose of this work to improve the performance-limiting Teflon-bonded carbon cathode and to gain mechanistic insights which will suggest further refinements in technology. The present work was performed using a neutral lithium chloro-aluminate solution (1.5 molar), in which lithium anodes are fairly stable, and which is, therefore, suitable for primary cell use. As is the situation for the analogous thionyl chloride systems, acidic (e.g.,  $AlCl_3$ -rich) solutions allow higher voltages and cathode service life under load, but are suitable only for reserve cell use.

## EXPERIMENTAL PROCEDURES

### Preparation of Electrolyte

Sulfuryl chloride was refluxed over lithium ribbon for several hours and then distilled under a positive pressure of argon, retaining the middle fraction. Lithium aluminum chloride was prepared by fusion of the salts as described previously.<sup>5</sup> The 1.5 M solutions were prepared in an argon atmosphere, in a glove box, and were stored in a tightly stoppered bottle. Electrolyte was used within a day of preparation or argon-degassed just before use.

### Preparation of Cathodes

"uncompressed" cathodes were prepared, as described previously,<sup>6</sup> by wet-blending of DuPont TFE-30 emulsion, carbon powder, and a sufficient amount of water to yield a stiff paste. The latter was then applied to a 2.5 cm x 2 cm Exmet (Exmet Corp.) support. The support was prepared by welding 2 thicknesses

<sup>1</sup>G. E. Blomgren and M. L. Kronenberg, German Patent 2,262,756 (1973).

<sup>2</sup>J. J. Auborn, R. D. Bezman, K. W. French, A. Heller, and S. F. Lieberman, "Lithium Batteries Based On Inorganic Electrolytic Solutions," Proc. of 26th Power Sources Symposium, p. 45 (1974).

<sup>3</sup>S. Gilman, "An Overview of the Primary Lithium Battery Program," Proc. of 26th Power Sources Symposium, p. 29 (1974).

<sup>4</sup>J. J. Auborn and N. Marincic, Power Sources 5, edited by D. H. Collins, Academic Press, London (1975), p. 683.

<sup>5</sup>W. K. Behl, J. Christopoulos, M. Ramirez, and S. Gilman, J. Electrochem. Soc. 120, 1619 (1973).

<sup>6</sup>W. K. Behl, et al., *ibid.*

of (Type 5 Ni7-2/0) screen together, with the mesh out of registration so as to provide maximum tortuosity for good anchoring of the Teflon-carbon mixture and to provide high electronic conduction. While still moist, the electrode was pressed to whatever thickness (depending on the particular carbon powder used) required for a final thickness of 0.035 "±0.002" after vacuum-drying for approximately 24 hours at 99°C.

"Compressed" (the fabrication procedure finally developed for United Carbon) cathodes were prepared as described above, but compressed to an intermediate thickness of 0.0615" while still moist. After vacuum drying, the electrode was pressed in a 0.025" frame and after re-expansion had a final thickness of 0.035". The "uncompressed" electrodes made with Shawinigan black or Darco G-60 were of good, uniform appearance and possessed good adherence after the vacuum drying step. The uncompressed electrodes made of Columbia or United Carbon black were badly cracked and fragile after the drying stage. The compressed United Carbon electrodes presented a good appearance and were sturdy.

#### Preparation of Cells

Cells were assembled in an all-Teflon jig with the plane of the electrodes parallel to the bottom of the jig. The cathode was placed between two lithium anodes. A lithium foil electrode placed in the same plane as the cathode served as the reference electrode. A 0.012" thick glass "filter-paper" provided mechanical separation between the cathode and the lithium counter-electrodes, facing it on each side. The lithium anodes were fabricated by pressing nickel Exmet into a 0.050" thick lithium foil. After assembling the cell and adding electrolyte, a Teflon weight was applied to the cell to help maintain good contact between the cell components. Electrical connections were made to the platinum wires sealed in the cap of a glass outer container having a standard taper ground glass joint and the cell assembly was then enclosed in the outer container. All assembly steps were accomplished in the glove box.

#### Electrochemical Measurements

Discharge and polarization curves were recorded on a Moseley Strip Chart Recorder at 22  $\pm 2^\circ\text{C}$ . The discharge curves were obtained while applying constant current from a power supply. The polarization curves were measured by applying predetermined constant currents (starting from 0.02 mA/cm<sup>2</sup>) for a period of three minutes before recording each cathode potential.

#### Cathode Porosity Determination

The percent porosity is defined as the percent of wet cathode volume available for absorption of SO<sub>2</sub>Cl<sub>2</sub>. The volume of SO<sub>2</sub>Cl<sub>2</sub> absorbed was determined by weighing a cathode before and after immersion in SO<sub>2</sub>Cl<sub>2</sub> and "blotting" on a glass surface. The wet volume of the cathode was determined by measuring its lineal dimensions with calipers. The porosity measurements were conducted in the glove box.

#### Chemical Analysis

The solubility of lithium chloride at 25°C in SO<sub>2</sub>Cl<sub>2</sub> was determined by preparing a saturated solution at 30°C, allowing equilibration/precipitation

to proceed for several days at 25°C, and then weighing the lithium chloride residue after taking 10 cc of solution to dryness.

Determination of sulfonyl chloride-insoluble chloride in discharged cathodes was accomplished as follows. The cathode was extracted with five 20 cc volumes of  $\text{SO}_2\text{Cl}_2$  (with vigorous magnetic stirring) during a 24-hour period. The cathode was then vacuum dried, first at room temperature, and then at 100°C. The cathode was then extracted with a total volume of 100 cc of water and aliquots of the extract titrated potentiometrically with a standardized silver nitrate solution.

Aluminum was determined quantitatively to correct for occluded lithium aluminum chloride in the sulfonyl chloride-insoluble (lithium) chloride cathode product residue. The aurintricarboxylate colorimetric method<sup>7</sup> was employed, and aluminum concentrations read off from a Beer's Law plot at the absorption maximum of 525 m $\mu$ .

#### Volumetric Determination of $\text{SO}_2$ Gas Release During Cell Discharge

The cell was prepared for discharge as described above. Before use, a volume of electrolyte was pre-saturated with  $\text{SO}_2$  for 45 minutes by bubbling the gas through the solution. After assembling the cell and closing the gas-tight glass outer envelope, the latter was flushed with  $\text{SO}_2$  through its two stopcocks. The glass envelope was then connected to a manifold and gas buret assembly by means of standard taper joints. Before opening the stopcock separating the cell from the manifold-buret assembly, the latter was evacuated and back-filled with  $\text{SO}_2$ . Measurements were made more or less frequently depending on observed rate of change of volume and a rate of gas release derived from each pair of adjacent volume determinations.

#### Determination of Solubilities of $\text{SO}_2$ and $\text{Cl}_2$ in $\text{SO}_2\text{Cl}_2$

In an alkaline aqueous solution,  $\text{SO}_2$  or  $\text{Cl}_2$  when individually dissolved, can be titrated through iodimetry or iodometry, respectively.<sup>8</sup> If both gases are introduced into an alkaline solution, they will react, resulting in quantitative oxidation of the  $\text{SO}_2$ , by  $\text{Cl}_2$ , to  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  plus the balance of the component present in higher normality. Therefore, only the excess of equivalents may be determined iodometrically/iodimetrically for such a mixture. Pure sulfonyl chloride can be expected to behave like a stoichiometric mixture of  $\text{SO}_2$  and  $\text{Cl}_2$  when dissolved in an alkaline solution, as was confirmed.

Solutions of either gas in  $\text{SO}_2\text{Cl}_2$  were prepared by bubbling the gas through the liquid for 1/2 hour. A 1 cc aliquot of either of the solutions was then placed in an ampoule which was supported above 40 cc of 1.5 M aqueous KOH solution in a flask with a gas-tight stopper. The ampoule was dropped into the KOH solution and the latter shaken vigorously. A sample of argon-saturated  $\text{SO}_2\text{Cl}_2$  gave a negligible iodimetric or iodometric blank determination. Iodimetric/iodometric determinations were conducted on the saturated solutions of the pure gases.

<sup>7</sup> E. B. Sandell, Colorimetric Determination of Traces of Metals (Interscience Publishers, Inc., New York, 1950), p. 146.

<sup>8</sup> I. M. Kolthoff and E. G. Sandell, Textbook of Quantitative Inorganic Analysis (The Macmillan Co., N.Y., 1948), p. 614.

## RESULTS AND DISCUSSION

### Dependence of Cathode Polarization and Discharge Capacity on Cathode Physical Properties

A Teflon content of 16% was chosen for preliminary comparative evaluation purposes because it was found to provide adequate coherence of the Teflon-carbon mixtures and adherence to the screens even though it is not the optimum Teflon loading for each individual carbon powder.

Table 1 identifies the carbon powders used in formulating cathodes, along with their Brunauer, Emmett, Teller (B.E.T.) surface areas. Shawinigan black possesses the lowest area of the entries listed, but has been a frequent choice of lithium battery technologists because of its good mechanical working properties and porosity. The latter quality is due, in part, to its extensive chain-like microstructure. Darco G-60 is a relatively high-area activated charcoal. The United and Columbia carbon blacks listed, possess particularly high surface areas and were originally produced for use in experimental aqueous primary cells.<sup>9,10</sup>

The cathodes were compared at the same thickness (0.035") (rather than at the same weight) since that allows the best comparison with respect to overall performance of a practical cell. The carbon loadings obtained reflect the different packing tendencies of the Teflon-carbon mixtures when accommodating to the same volume. Previous studies revealed that the B.E.T. surface area of such electrodes is approximately the same as that of the original carbon utilized.<sup>11</sup> On that basis, Table 1 presents the B.E.T. areas for the electrodes computed from the powder areas and the carbon loadings (of representative electrodes). Because the variations in carbon loadings of the electrodes tend to compensate for the variations in surface areas of the powders, the only large variation in electrode B.E.T. area is that for Shawinigan black when compared with the other three carbons.

The electrode porosity, or more precisely - the ability to absorb  $SO_2Cl_2$ , depends on the original microstructure of the powder and its interaction with the Teflon binder. As already mentioned above, the latter properties are particularly favorable for Shawinigan black and probably account for the higher than average cathode porosity listed in the table and the fact that the electrodes have a sturdy and uniform appearance. The Darco cathodes have the lowest porosity, and fair mechanical integrity. The Columbia and United carbon cathodes prepared by this method are cracked and fragile but possess medium porosity. When swollen with electrolyte, the latter electrodes acquired a more uniform appearance.

<sup>9</sup>M. T. Johnston, J. E. Smith, and M. J. Suber, "Carbon Black for Organic Depolarizer Batteries," Final Report, Contract DA-36-039-AMC-03239(E)(USAECOM), Columbian Carbon Company, (1964).

<sup>10</sup>J. B. Doe and D. B. Wood, "M-Dinitrobenzene Cell Performance," Proc 22nd Annual Power Sources Conference, p. 97 (1968).

<sup>11</sup>J. A. Christopoulos and S. Gilman, "Teflon-Bonded Cathodes in Lithium-Thionyl Chloride Cells," Proc. Tenth Intersociety Energy Conversion Engineering Conference, p. 437 (1975).

TABLE 1. CHARACTERISTICS OF TEFLON - BONDED CARBON CATHODES (16% TFE)

| TYPE OF CARBON               | DERIVATION                      | B.E.T. SURFACE AREA<br>OF CARBON: Meter <sup>2</sup> |                              | PER CM <sup>2</sup> OF<br>ELECTRODE GEO-<br>METRIC AREA* | PERCENT<br>ELECTRODE<br>POROSITY |
|------------------------------|---------------------------------|--|------------------------------|--|----------------------------------|
|                              |                                 | CARBON LOADING*                                      | PER GRAM OF<br>CARBON POWDER |  |                                  |
| SHAWINIGAN-50%<br>COMPRESSED | DECOMPOSITION OF<br>ACETYLENE   | 0.0194   | 66                           | 1.28   | 87                               |
| DARCO G-60                   | STEAM-ACTIVATION<br>OF CHARCOAL | 0.0048   | 301                          | 14.4   | 64                               |
| UNITED XC-6310-4             | DECOMPOSITION OF<br>OIL         | 0.0146   | 1000                         | 14.6   | 81                               |
| COLUMBIA HR 1670             | DECOMPOSITION OF<br>OIL         | 0.0104   | 1200                         | 12.5   | 75                               |

\*BASED ON (LENGTH X WIDTH) AREA OF ELECTRODE, ONE SIDE.

Figure 1 shows the polarization curves obtained for the four different carbon samples, with the recorded current density based upon the geometric cathode area (length X width, one side). From the practical point of view, it can be concluded that the United carbon would provide the best initial voltage in a practical cell, whereas Shawinigan black would provide the poorest.

The results of Figure 1 are re-plotted in Figure 2 but with the current densities computed from the total currents and the B.E.T. carbon areas of the electrodes. It is now apparent that polarization for three of the carbons (covering more than an order of magnitude's spread in B.E.T. area) is very similar in the range of currents where "activated" processes predominate. The Darco cathode shows significantly more polarization than the other three in that range. This may possibly be attributed to the fact that Darco G-60 is an "activated charcoal" with part of the B.E.T. area intragranular in nature and, consequently, not readily accessible to solid/liquid reactions. The steep decline of cathode potential at high current densities may be attributed (as applies also to the similar thionyl chloride cathode<sup>12,13</sup>) to transport limitations in pores partially blocked by a solid product of cell discharge.

Cathodes made from the four different carbon samples were discharged at a constant current density of 5 mA/cm<sup>2</sup> and the "full discharge capacities" determined from the discharge curves by drawing the appropriate tangents near the "knee" of the curves. In Figure 3, the capacities are plotted against the percent porosity values taken from Table 1. The relationship is approximately linear for the particular current density employed. The slope can be conceptualized as incorporating a pore "choking coefficient" as proposed by Marincic<sup>14</sup> for the thionyl chloride cathode. The similarity exists because the same major product of cathode reaction (LiCl) is involved in both cases, as discussed below. It may also be anticipated, as observed for the thionyl chloride cell,<sup>15</sup> that the distribution of LiCl in the cathode, and its effect on the discharge curve, will vary with the current density.

From Figures 1 and 3 it can be concluded that Shawinigan black affords the best cathode capacity but the poorest cathode voltage. United carbon black, which affords the highest cathode voltage performance, provides second-best capacity. The latter carbon black was selected for further experimentation.

#### Improvement of the United Carbon Cathode

Figure 4 presents discharge curves for experimental modifications of the cathode fabrication process (16% TFE) for comparison with those obtained by the original ("uncompressed") process (Curves 1 and 2). All cathodes were constructed to the same final thickness (0.035") but incorporated different

<sup>12</sup>J.A. Christopoulos and S. Gilman, *op. cit.*, p. 4.

<sup>13</sup>N. Marincic, *J. Appl. Electrochem.* 5, 313 (1975).

<sup>14</sup>N. Marincic, *ibid.*

<sup>15</sup>A. N. Dey and P. Bro, *J. Electrochem. Soc.*, 125, 1574 (1978).

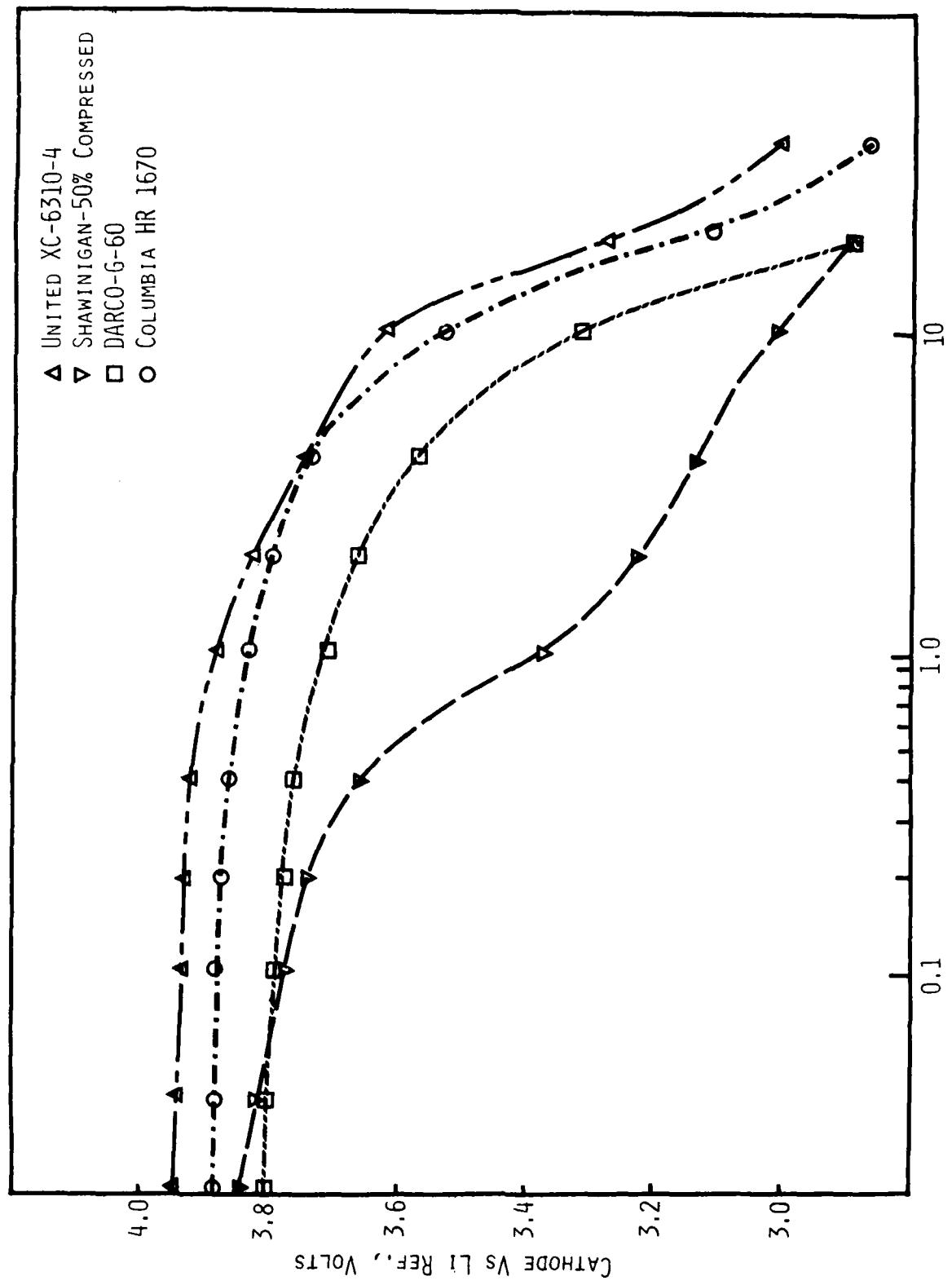


Figure 1. Polarization Curves for Teflon-Bonded Carbon Cathodes  
(16% TFE, Uncompressed)

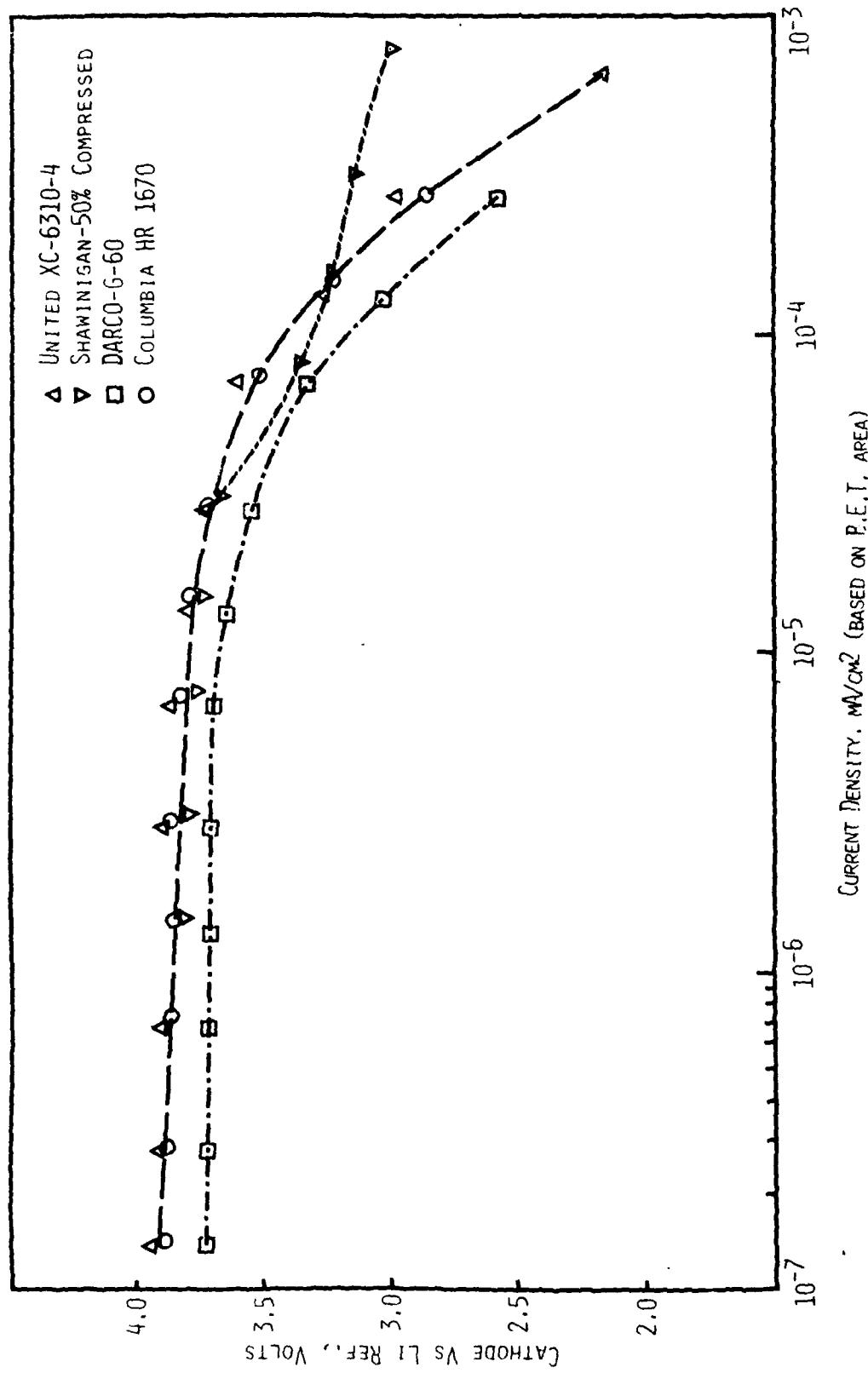


Figure 2. Polarization Curves for Teflon-Bonded Carbon Cathodes (16% TFE Uncompressed) Normalized With Respect to B.E.T. Area

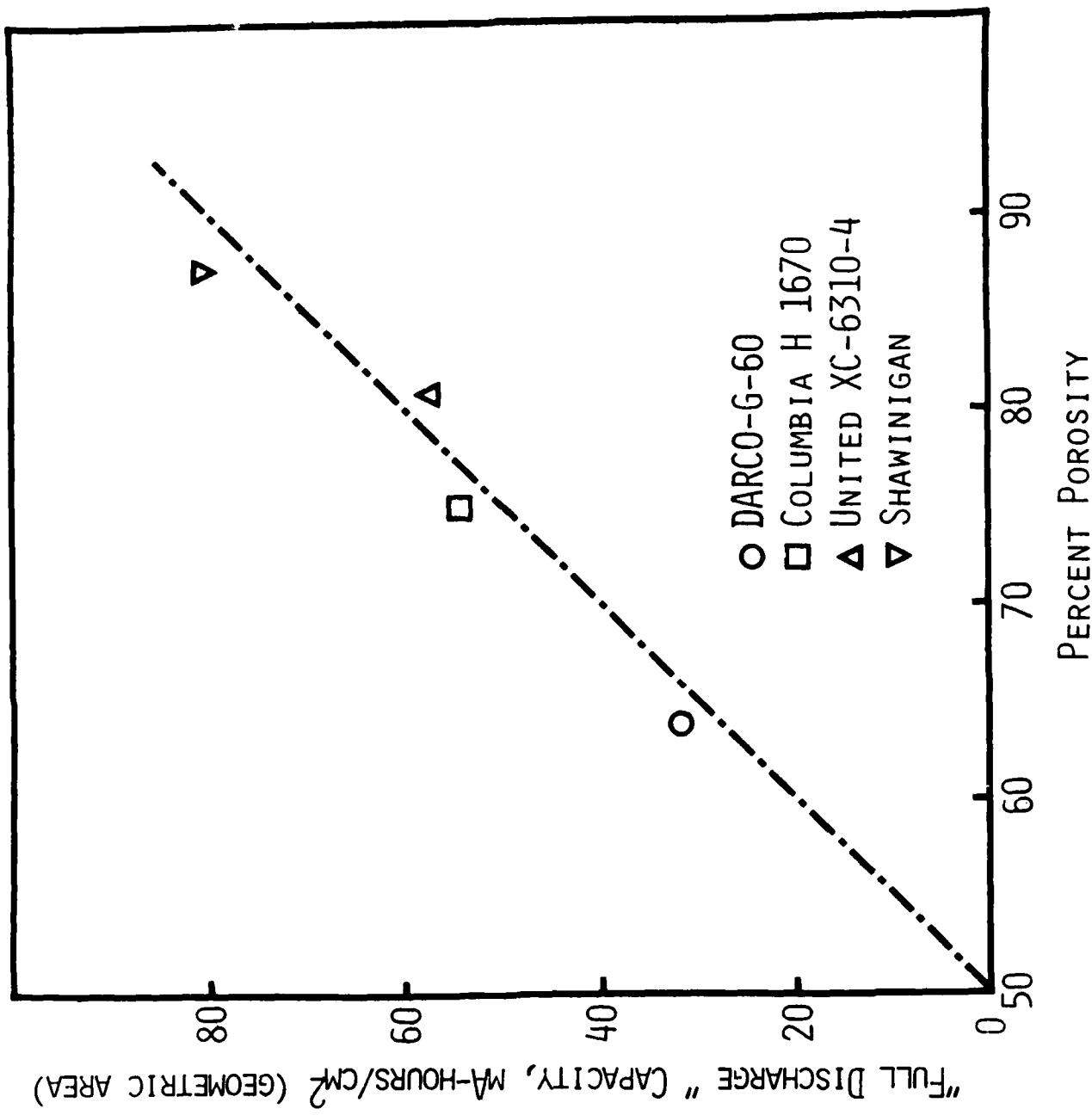


Figure 3. Capacity - Porosity Relationship for Teflon-Bonded Carbon Cathodes  
(16% TFE - Uncompressed)

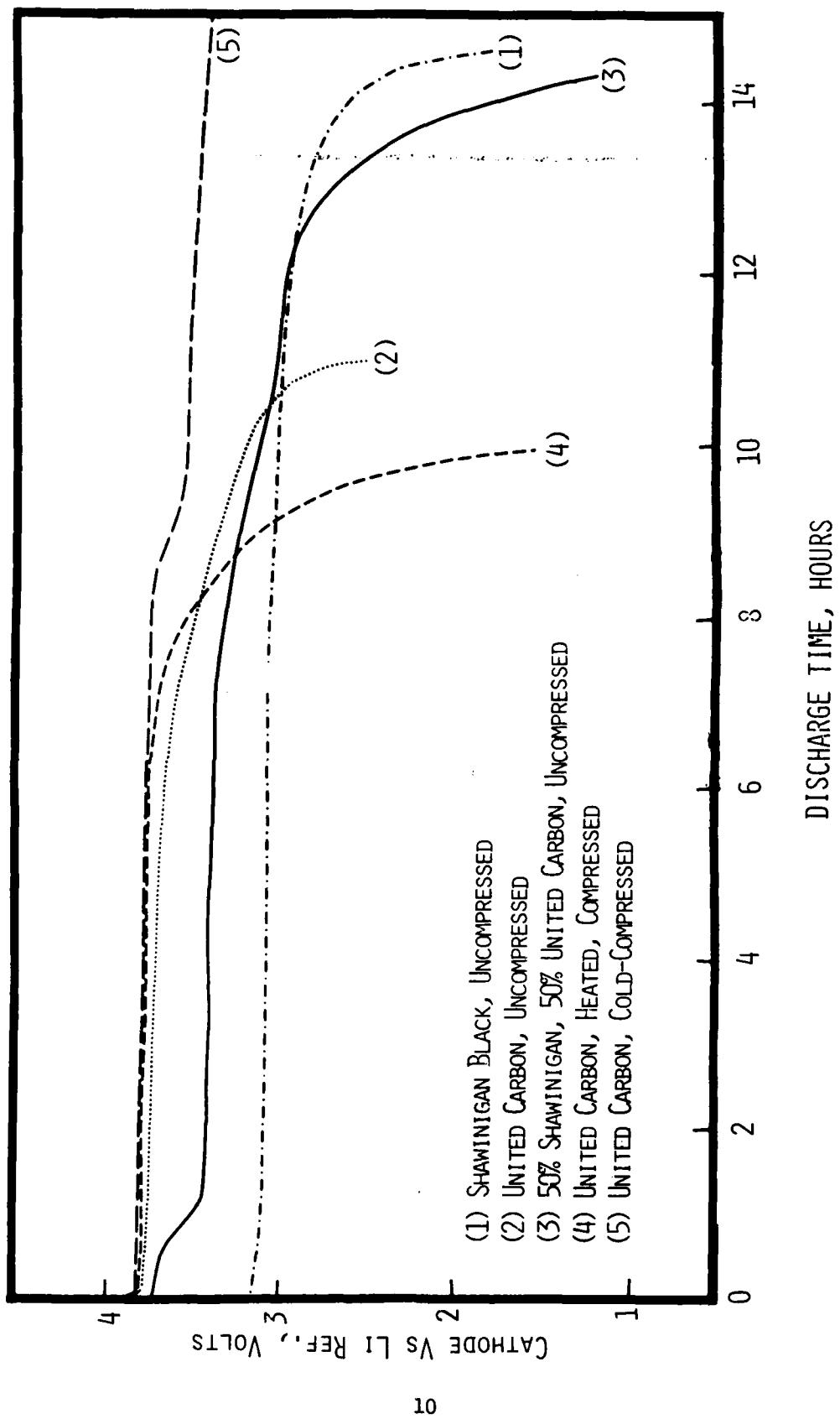


Figure 4. Discharge Curves ( $I = 5 \text{ mA/cm}^2$ ) for Differently-Formulated Cathodes

amounts of carbon. A mixture of the two carbons (Curve 3) results in the high capacity associated with Shawinigan black but only part of the increased voltage associated with United carbon black. Also, the physical integrity of the electrode is not good. Heat-compression of the United carbon cathode at 300°C (Curve 4) greatly improves its sturdiness and slightly improves the voltage, but causes decreased capacity. The "cold compression" process (Curve 5) results in a cathode of highest discharge voltage and longest life. This cold-compressed United carbon formulation was, therefore, selected for further optimization.

Figure 5 shows the discharge curves obtained, at a current density of 5 mA/cm<sup>2</sup>, for different concentrations of TFE in the dried United carbon Teflon mixtures. A maximum in cathode life ("full discharge capacity") is obtained for a TFE concentration of 10.7%. Duplicate runs for 9.7 and 10.7% are presented to show typical variation of results attributable to fabrication technique variability.

The 10.7% formulation was selected for the further investigations reported below. A typical electrode had a carbon loading of 0.024 g/cm<sup>2</sup> and a porosity of 87%. The electrode swelled 11% when immersed in electrolyte.

#### Solubilities of LiCl, SO<sub>2</sub> and Cl<sub>2</sub> in Sulfuryl Chloride

The solubility of LiCl in sulfuryl chloride at 25°C was determined to be less than 0.009 molar. This corresponds to a solubility product smaller than  $8 \times 10^{-5}$  and leads to the conclusion that LiCl is, practically speaking, insoluble in the 1.5 M lithium chloroaluminate concentration of our electrolyte.

The solubilities of Cl<sub>2</sub> and SO<sub>2</sub> at 24°C were determined to be 0.62 and 1.09 molal, respectively, when individually dissolved in pure SO<sub>2</sub>Cl<sub>2</sub>. The analysis for SO<sub>2</sub> correlates well with published results<sup>16</sup> for other temperatures.

#### Analysis of Cell Discharge Products

A discharged cathode, after rinsing in sulfuryl chloride and drying, was crushed and analyzed with an X-ray spectrometer. Diffraction lines were obtained for LiCl only. Two cathodes, A and B (formulated with 6.7 and 10.7% TFE, respectively), were discharged to a cut-off potential of 2 Volts, treated as described in the Experimental Section above and analyzed for both Cl<sup>-</sup> and Al<sup>3+</sup>. Table 2 presents the results of the analyses, assuming that all chloride in the cathode is either LiCl or LiAlCl<sub>4</sub>. It can be seen that agreement between the equivalents of charge passed and LiCl formed is within 2% which is taken as evidence that LiCl is the only ionic product of cathode discharge for the predominant discharge reaction. Quantitative precipitation of the LiCl in the cathode is a result of its insolubility, as already noted above. In this respect the situation is identical to that for thionyl chloride cells.<sup>17</sup>

<sup>16</sup>M. Aubry, B. Gilot, C. Jayles, *Annales Genie Chimique*, Vol 3, p. 33 (1967).  
<sup>17</sup>J. R. Driscoll, G. L. Holleck, and D. E. Toland, "Reactions in Lithium Thionyl Chloride Cells," *Proc. 27th Power Sources Symposium*, p. 28 (1976).

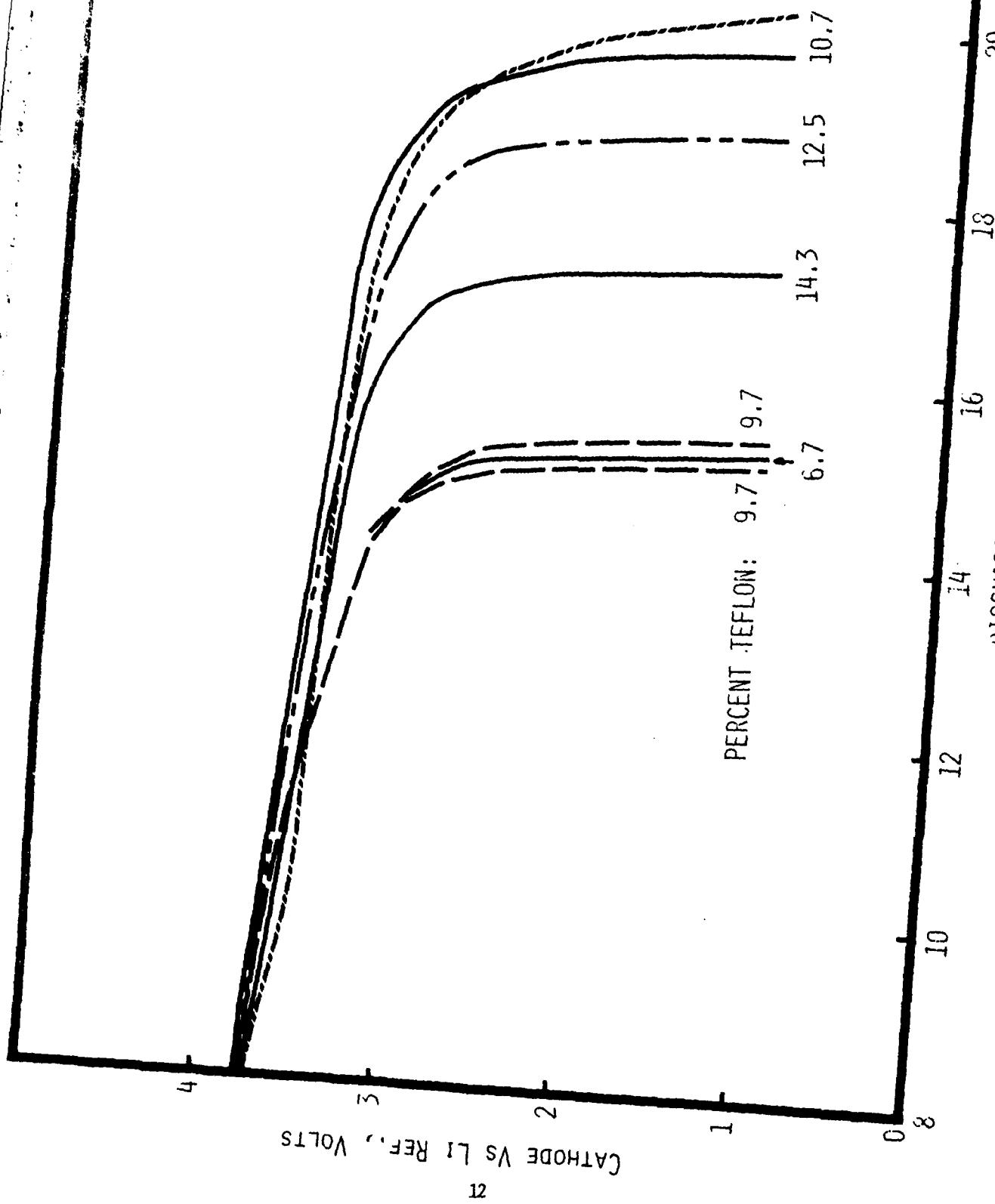


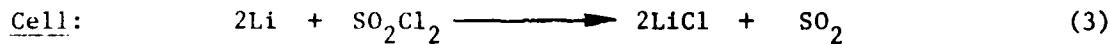
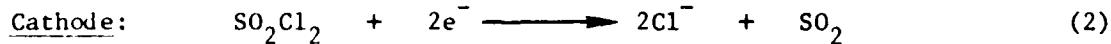
Figure 5. Discharge Curves ( $I = 5 \text{ mA/cm}^2$ ) for Cathodes Formulated With Varying Amounts of TFE (Uncompressed)

TABLE 2. CHLORIDE DETERMINATION FOR DISCHARGED CATHODES

|  | <u>Cathode A</u> | <u>Cathode B</u> |
|--|------------------|------------------|
| Total equivalents of $\text{Cl}^-$ determined argentrimetrically | 0.0146           | 0.02035          |
| 4 x equivalents of $\text{Al}^{+3}$ determined colorimetrically  | 0.00093          | 0.00103          |
| Equivalents of $\text{Cl}^-$ as $\text{LiCl}$                    | 0.0137           | 0.0193           |
| Equivalents of electricity consumed in cathode discharge         | 0.0141           | 0.0189           |

One of the possible non-ionic products of cell discharge is elemental sulfur, as proposed previously.<sup>18</sup> A cathode was fully discharged (20 hours) at a current density of 5 mA/cm<sup>2</sup>. Extraction of the vacuum-dried cell components with  $\text{CS}_2$  yielded only 15 mg of a yellow waxy substance with no distinct melting point. The substance dissolved in benzene and, therefore, was apparently not sulfur.

The most simple cell discharge reaction involving  $\text{LiCl}$  as the ionic product would produce  $\text{SO}_2$  as the neutral product. Cells were always observed to develop positive pressure during discharge. The resulting gas phase contained  $\text{SO}_2$  and  $\text{Cl}_2$  which are, in any case, present above an  $\text{SO}_2\text{Cl}_2$  volume.<sup>19</sup> To avoid the difficulty of analyzing for  $\text{SO}_2$  released in the presence of  $\text{Cl}_2$ , volumetric determination of gas release during discharge was made after saturating the solution with  $\text{SO}_2$ . This procedure has the benefit of suppressing  $\text{Cl}_2$  release while forcing electrochemically produced  $\text{SO}_2$  into the gas phase. The results of a determination appear in Figure 6. The figure compares the observed rate of gas production with that anticipated based on the reactions:



$$E^\circ = 3.909 \text{ Volts (30}^\circ\text{C)}$$

<sup>18</sup>J. J. Auborn, et al., op. cit., p. 1.

<sup>19</sup>Encyclopedia of Chemical Technology, K. Othmen, Ed., Vol. 14, p. 398 (1969).

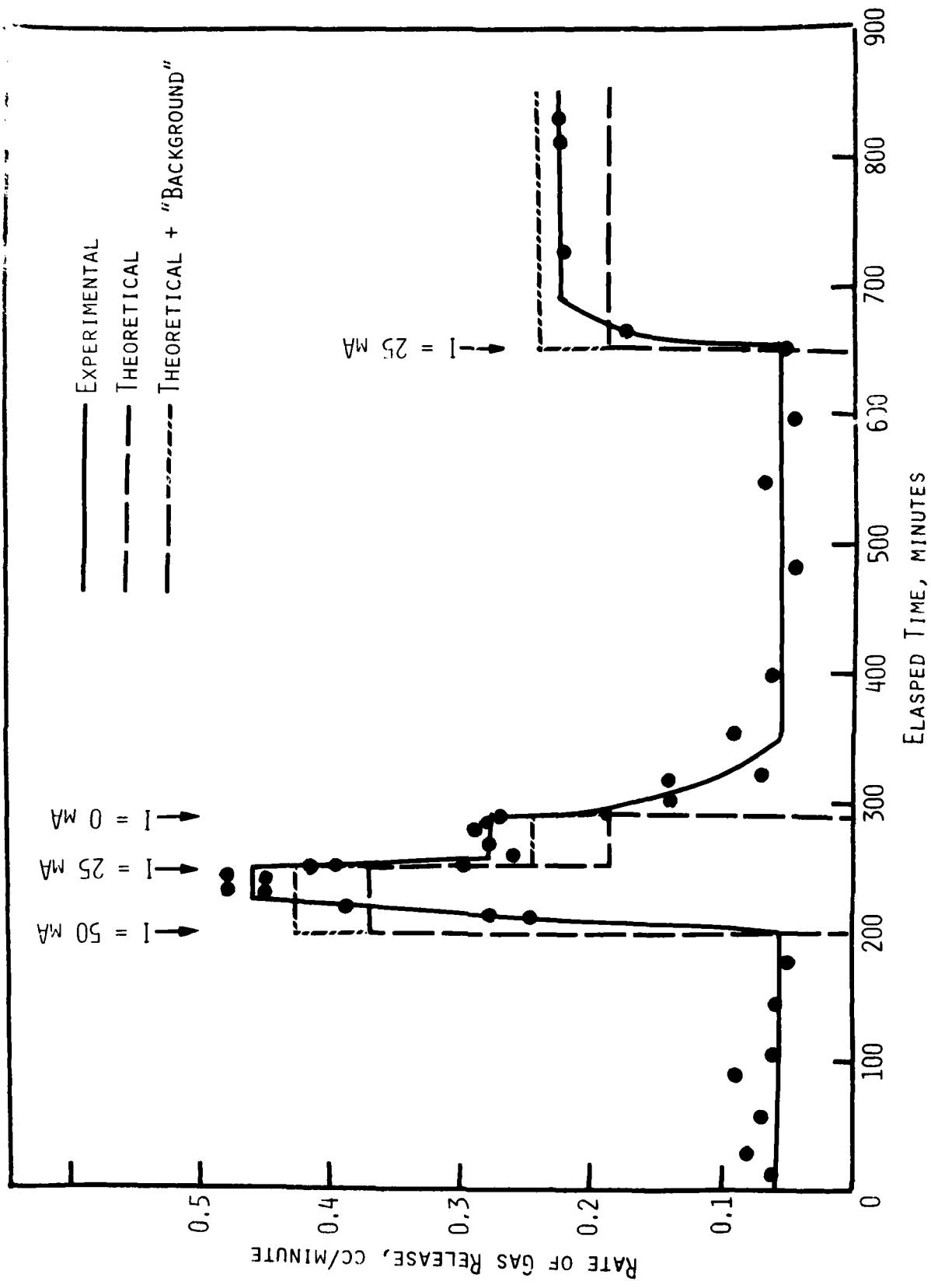


Figure 6. Gas Release During Cathodic Reduction of  $\text{SO}_2\text{Cl}_2$

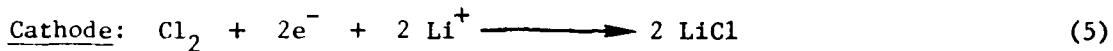
A "background" production of gas of approximately 0.06 cc/minute was measured at open circuit. That "background" may, for instance, correspond to initial reaction (corrosion) of the fresh lithium electrode surface with the solvent. When the "background" and theoretical rates are added, they compare fairly well with the experimental rates eventually established when the current is increased or decreased. The results imply that the cell reactions proceed, at least largely, according to Equations (1) and (2).

#### Effect of Dissolved Gases on Cathode Discharge

Sulfuryl chloride dissociates readily into  $\text{SO}_2$  and  $\text{Cl}_2$  and that reaction may be suspected of playing a role in the cell electrochemistry. The equilibrium constant at  $30^\circ\text{C}$  is 0.0288 for the reaction:<sup>20</sup>



The chlorine produced by Equation (4) could then be consumed as follows:



The standard potential,  $E^\circ$ , for Equation (5) vs a lithium reference electrode is 3.979 Volts ( $30^\circ\text{C}$ ). However, the activity of  $\text{Cl}_2$  in solution will always be equal to or less than dictated by the equilibrium constant of Equation (4), and, therefore, always lower than unity. Correspondingly, the cell potential can never exceed that of Equation (3) unless molecular  $\text{Cl}_2$  is introduced from an external source.

Equation (4) could proceed either homogeneously or heterogeneously. However, for pure  $\text{SO}_2\text{Cl}_2$ , the homogeneous reaction is slow, while the heterogeneous decomposition is relatively rapid at a carbon surface.

Figure 7 compares the polarization curves obtained when the electrolyte is saturated with either argon,  $\text{SO}_2$ , or  $\text{Cl}_2$ . Results for solutions prepared in the glove box and stored for a few days resemble the "argon-saturated" example. Clearly,  $\text{Cl}_2$  and  $\text{SO}_2$  serve to enhance or diminish the current, respectively, at any particular cathode potential. The effect of  $\text{Cl}_2$  saturation demonstrates that molecular  $\text{Cl}_2$  is kinetically more active than  $\text{SO}_2\text{Cl}_2$  in this electrolyte although reduction occurs well below the appropriate thermodynamic cell potential (3.979 Volts). Since  $\text{SO}_2$  is itself not reduced at these high potentials, and since it could not produce any significant decrease in  $\text{Cl}_2$  bulk concentration over that in the argon-saturated solution, it is proposed that it exerts its effect on the polarization curve by decreasing the surface concentration of the chlorine which (at moderate currents and high potentials) normally serves as an intermediate in the reduction of  $\text{SO}_2\text{Cl}_2$ . In practical situations (small volume of electrolyte, extended periods of discharge), the electrolyte will become  $\text{SO}_2$ -rich and the tendency for the results for the argon and  $\text{SO}_2$ -saturated electrolytes to converge (at higher currents) is also apparent from the figure.

<sup>20</sup> Encyclopedia of Chemical Technology, op. cit., p. 13.

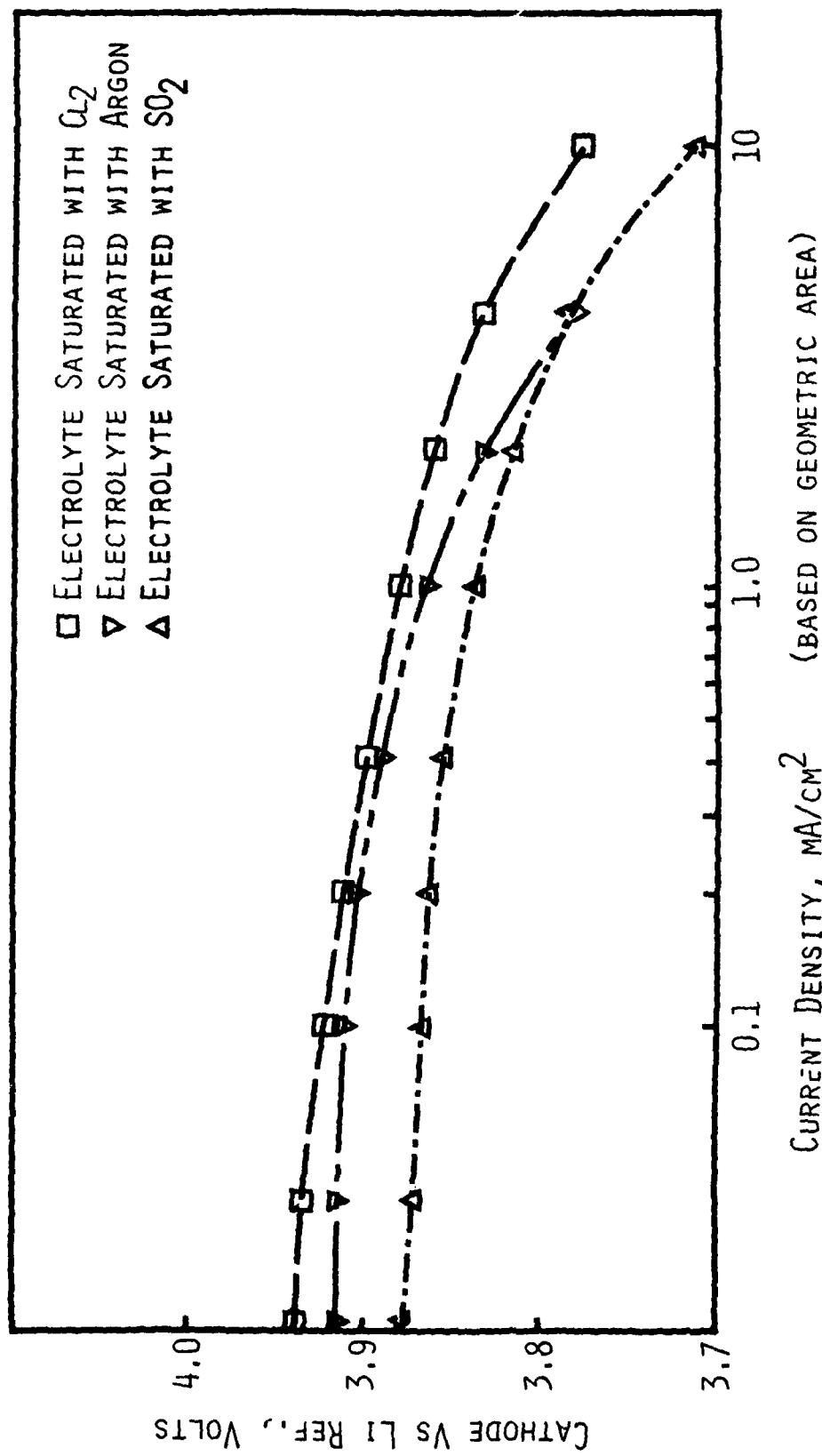


Figure 7. Cathode Polarization Curves for Optimized Cathode Electrolyte Pre-Saturated with Different Gases

Discharge curves (constant current of 5 mA/cm<sup>2</sup>) appear in Figure 8. The results for the SO<sub>2</sub>-saturated, argon-saturated, and "aged" electrolytes are almost indistinguishable in the first few hours (as might be expected due to buildup of product SO<sub>2</sub>) in the first two cases. The variations during the later period of discharge are within the normal span for any particular (e.g., argon-saturated) starting condition. The significantly shorter discharge for Cl<sub>2</sub>-saturation was found reproducible. A possible explanation is that the direct reduction of chlorine from the bulk of the solution occurs near the outer surface of the electrode and has a greater tendency to clog pores than the heterogeneously produced Cl<sub>2</sub> intermediate which would be produced and consumed throughout the electrode volume.

The discharge curves for cells with either argon/SO<sub>2</sub>-saturated or "aged" electrolyte exhibit an intermediate voltage decline suggesting a two-step reduction. This is probably analogous to the two-wave reduction observed by Behl<sup>21</sup> during voltage-sweep studies of carbon microelectrodes. Behl attributed the first and second waves to reduction of Cl<sub>2</sub> and undissociated SO<sub>2</sub>Cl<sub>2</sub>, respectively. A similar interpretation for the second transition in the discharge curve is tentatively adopted here. The transition to reduction of molecular SO<sub>2</sub>Cl<sub>2</sub> might come about as the available surface area available to catalyze SO<sub>2</sub>Cl<sub>2</sub> dissociation is diminished through coating with product LiCl.

#### Dependence of Discharge Curves (Optimized United Carbon Cathodes) On Electrolyte Volume and Current Density

Figure 9 presents discharge curves for several current densities at the "standard" ratio of electrolyte volume to cathode geometric area of 1 ml per cm<sup>2</sup>. As for thionyl chloride cells, the efficiency of cathode utilization tends to drop off with increased current density. The relatively efficient discharge current density of 2 mA/cm<sup>2</sup> was selected for exploring the effect of varying the electrolyte volume. Curves for several different volume/area ratios appear in Figure 10. From such curves, a charge Q was estimated for "full discharge" and for discharge to a first "high voltage" transition point. The results are plotted in Figure 11. Based on Equation (3), the values of charge, and the volume of solution in the cell, a "percent solvent utilized" was derived and plotted in Figure 11. For volume/area rates of 0.14 or less, cell components are visibly incompletely wetted at the beginning of the experiment. No attempt has yet been made to analyze the rather sharp dependence on electrolyte volume/area ratio. Maximum solvent utilizations at "high voltage" and for "full discharge" were not observed to exceed 20 and 30%, respectively.

Let us consider how the 20% "high voltage" efficiency compares with the percentage of equivalents of Cl<sub>2</sub> available from the dissolved phase only. Corresponding to the Cl<sub>2</sub> (0.62 molal, as reported above) in a saturated solution at 24°C, 7.8% of the reducible equivalents are available from pre-dissolved Cl<sub>2</sub>. For de-gassed sulfonyl chloride, allowed to dissociate to equilibrium with the gas phase, the partial pressure of Cl<sub>2</sub> is approximately 0.05 atmosphere (based on the vapor pressure of SO<sub>2</sub>Cl<sub>2</sub> and dissociation constant of SO<sub>2</sub>Cl<sub>2</sub> at 30°C).<sup>22</sup>

<sup>21</sup>W. K. Behl, J. Electrochem. Soc., 127, 1444 (1980).

<sup>22</sup>Encyclopedia of Chemical Technology, op. cit., p. 13.

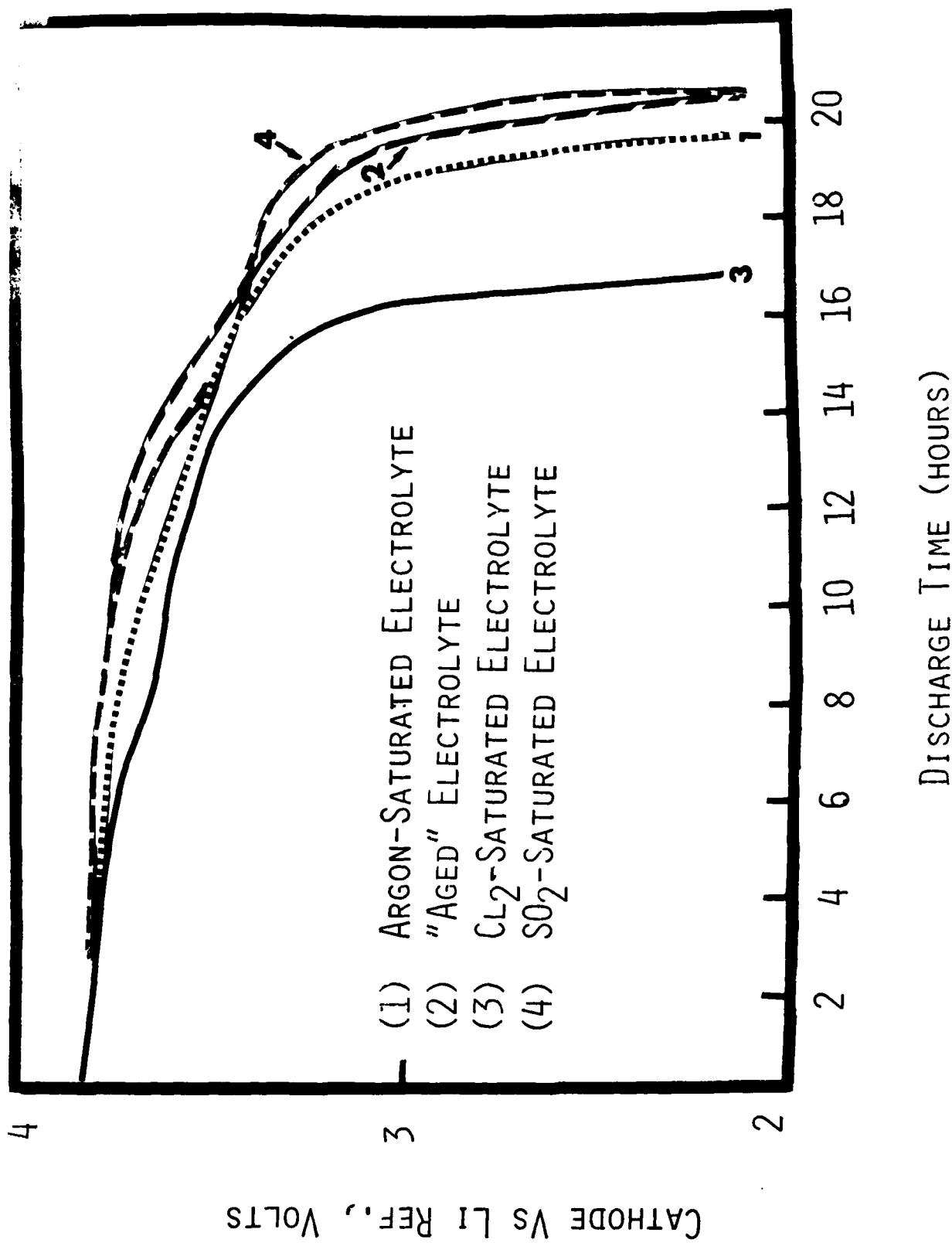


Figure 8. Cathodic Discharge Curves ( $I = 5 \text{ mA/cm}^2$ ).  
 Electrolyte Saturated with Different Gases

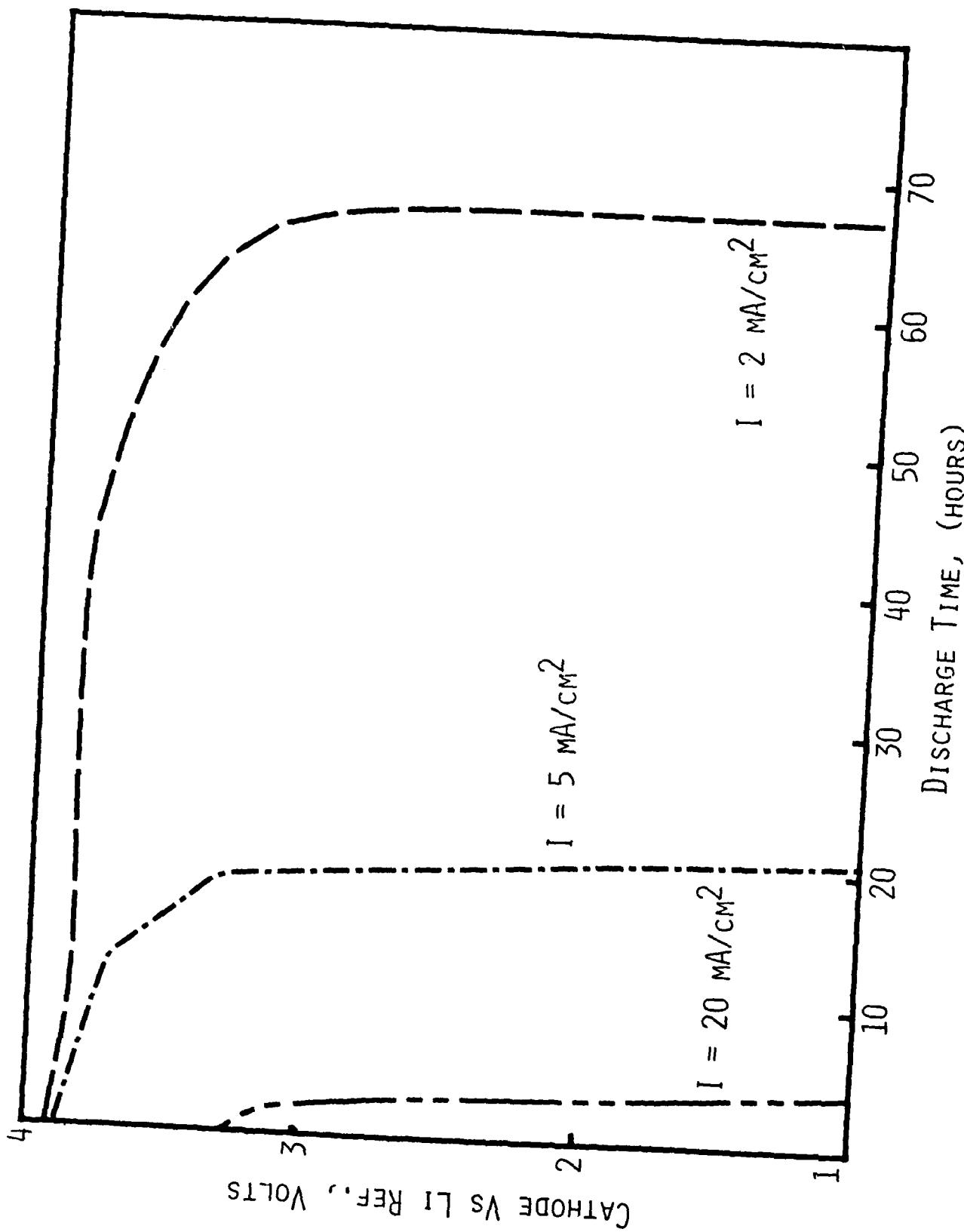


Figure 9. Discharge Curves for Optimized Cathode

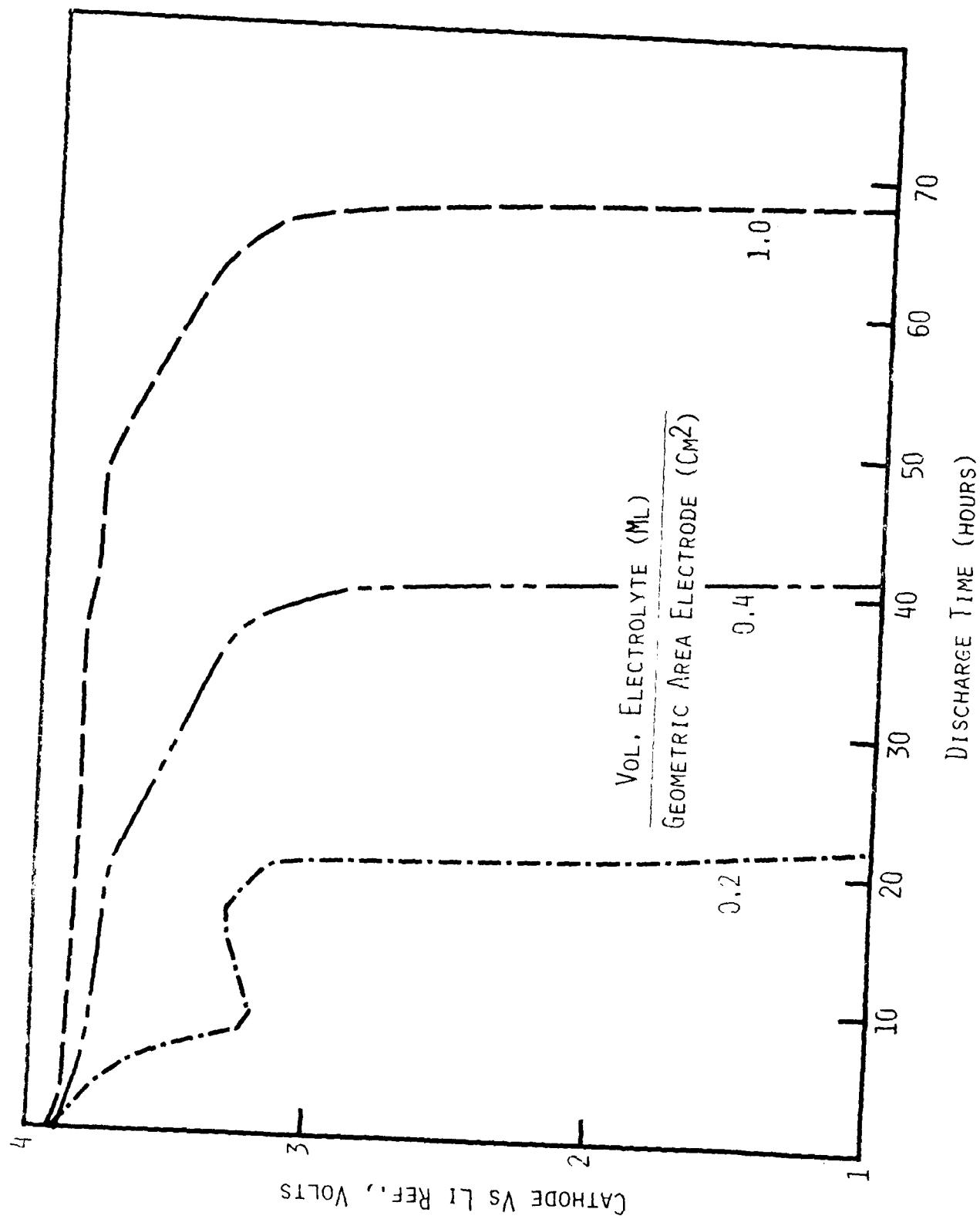


Figure 10. Discharge Curves for Optimized Cathode Using Various Volumes of Electrolyte

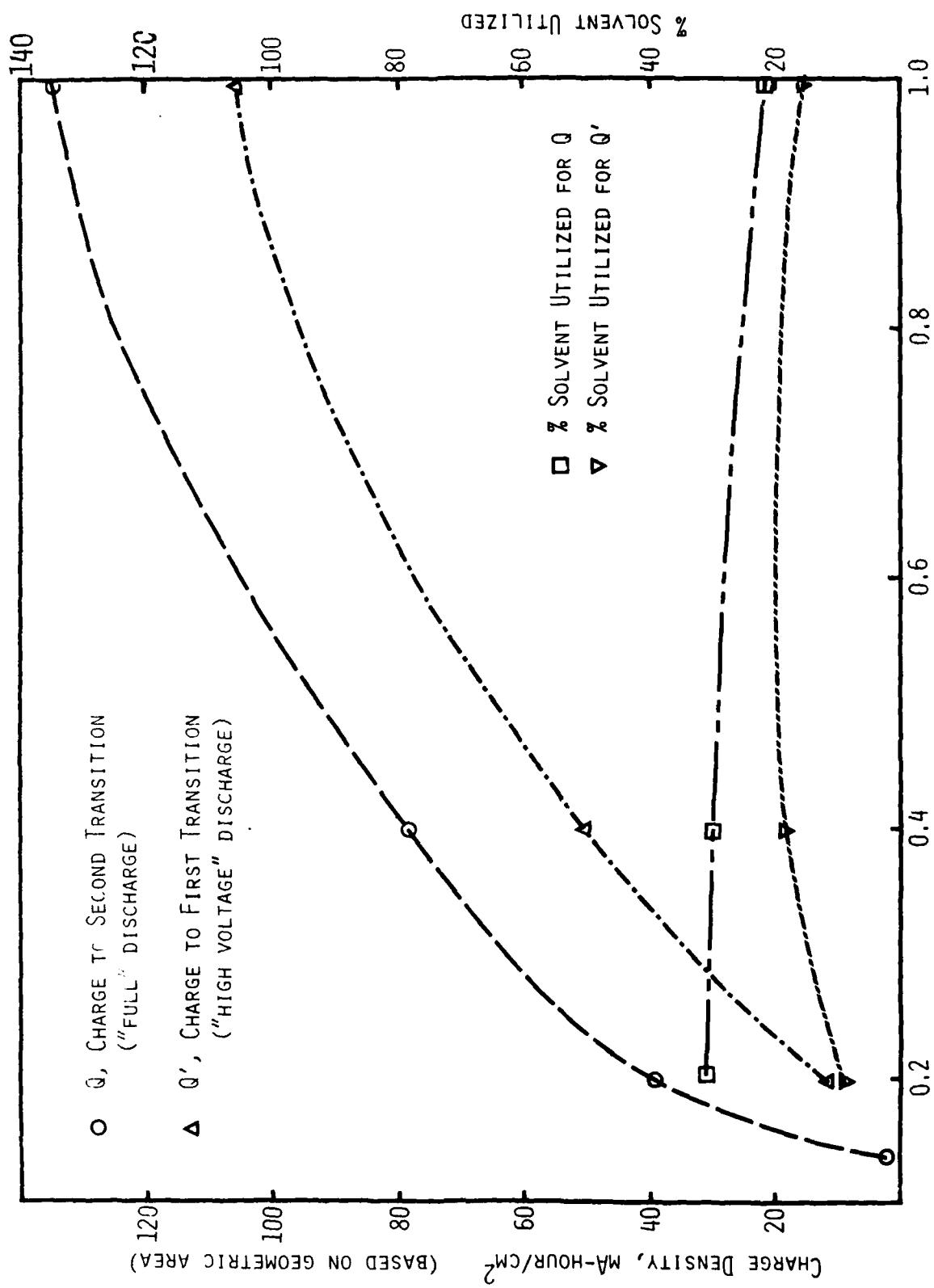


Figure 11. Dependence of Cathodic Charge and Solvent Utilization on Electrolyte Volume

The corresponding percentage of equivalents available from  $\text{Cl}_2$  can be as low as 0.4% (if Henry's Law is obeyed). Hence, the "high voltage" solvent utilization reported above cannot be attributed to a "reservoir" of  $\text{Cl}_2$  resulting from dissociation of the solvent before cathodic discharge is begun; the chlorine must be supplied during the cathodic process.

#### Comparison of $\text{SO}_2\text{Cl}_2$ with $\text{SOCl}_2$ Cathodes

The polarization and discharge curves are compared in Figures 12 and 13, respectively, for cathodes utilizing  $\text{SOCl}_2$  and  $\text{SO}_2\text{Cl}_2$ . Shawinigan black cathodes were used as representing the "state-of-the-art" for  $\text{SOCl}_2$  and the optimized United carbon cathodes were utilized for  $\text{SO}_2\text{Cl}_2$ . It can be seen from the figures that  $\text{SO}_2\text{Cl}_2$  appears to offer an advantage in terminal voltage over  $\text{SOCl}_2$  at high current densities, if the optimized cathodes are utilized.

#### CONCLUSIONS

Teflon-bonded carbon cathodes were fabricated using a variety of carbon powders with specific surface areas ranging from 66 to 1200 meter<sup>2</sup>/gram. When functioning as a sulfonyl chloride reduction cathode in a solution of neutral lithium chloroaluminate, the polarization of the Teflon-bonded electrode is a direct function of the B.E.T. surface area of the carbon it contains. The service life of a cathode is a function of its porosity, the latter determining its ability to accommodate to the solid product of cathodic discharge. By adjusting the fabrication procedure, a cathode (utilizing United carbon black) was developed which simultaneously incorporates high active area and high porosity and, therefore, provides long life and high cathode potential under load.

When operating at room temperature and at moderate current densities, the optimized Teflon-bonded carbon cathode was found to produce  $\text{LiCl}$  as the sole solid product of reaction. The  $\text{LiCl}$  is quantitatively deposited within the pores of the cathode. Volumetric measurements of gas release suggest that  $\text{SO}_2$  is the other product of the cathodic discharge process. The results of polarization measurements made with the optimized cathodes using chlorine or sulfur dioxide-saturated electrolyte suggest that cathodic reduction of  $\text{SO}_2\text{Cl}_2$  at moderate current densities proceeds through the reduction of chlorine released by the carbon catalyzed decomposition of  $\text{SO}_2\text{Cl}_2$ .

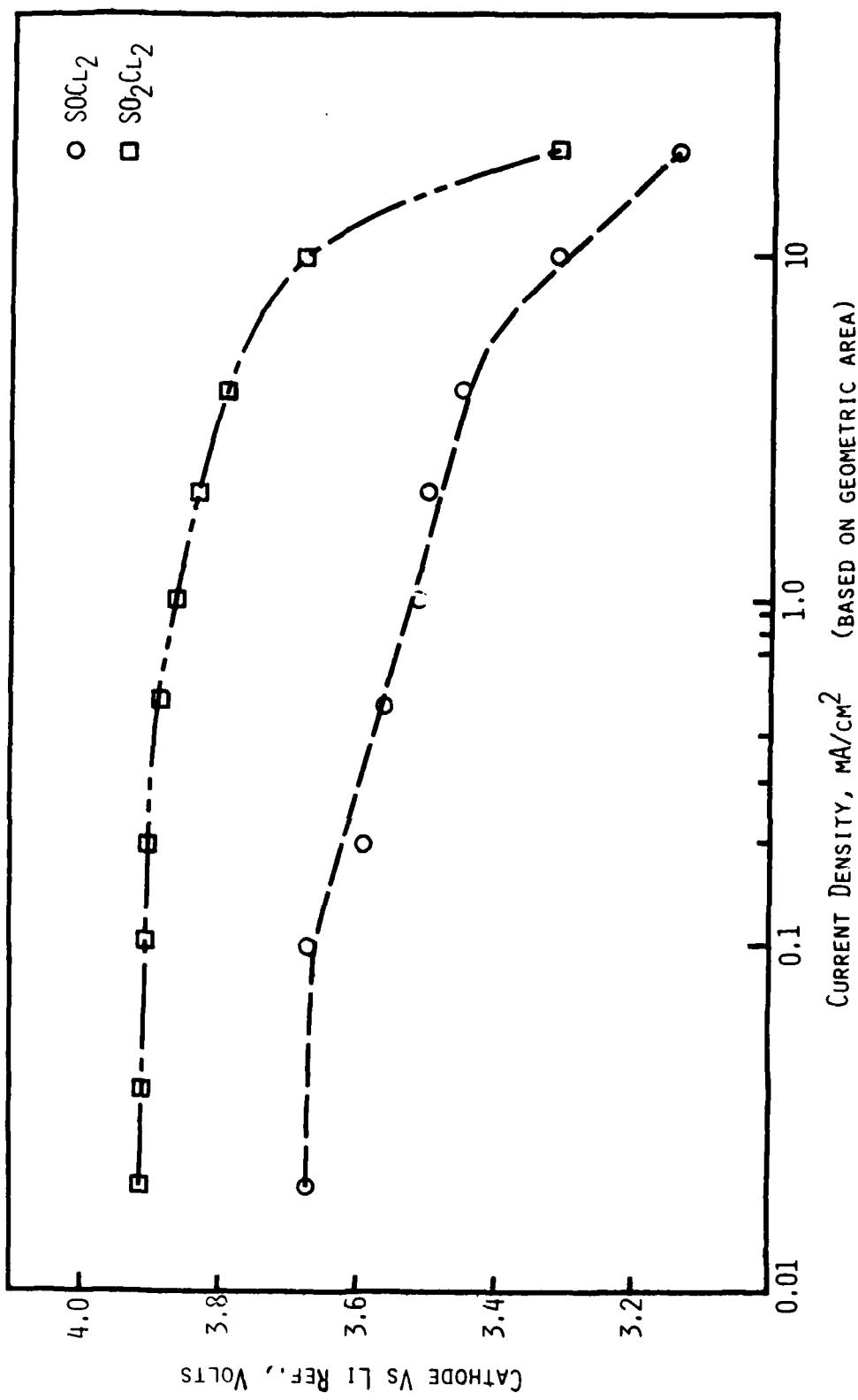


Figure 12. Comparison of Cathodic Polarization Curves for  $\text{SO}_2\text{Cl}_2$  and  $\text{SOCl}_2$

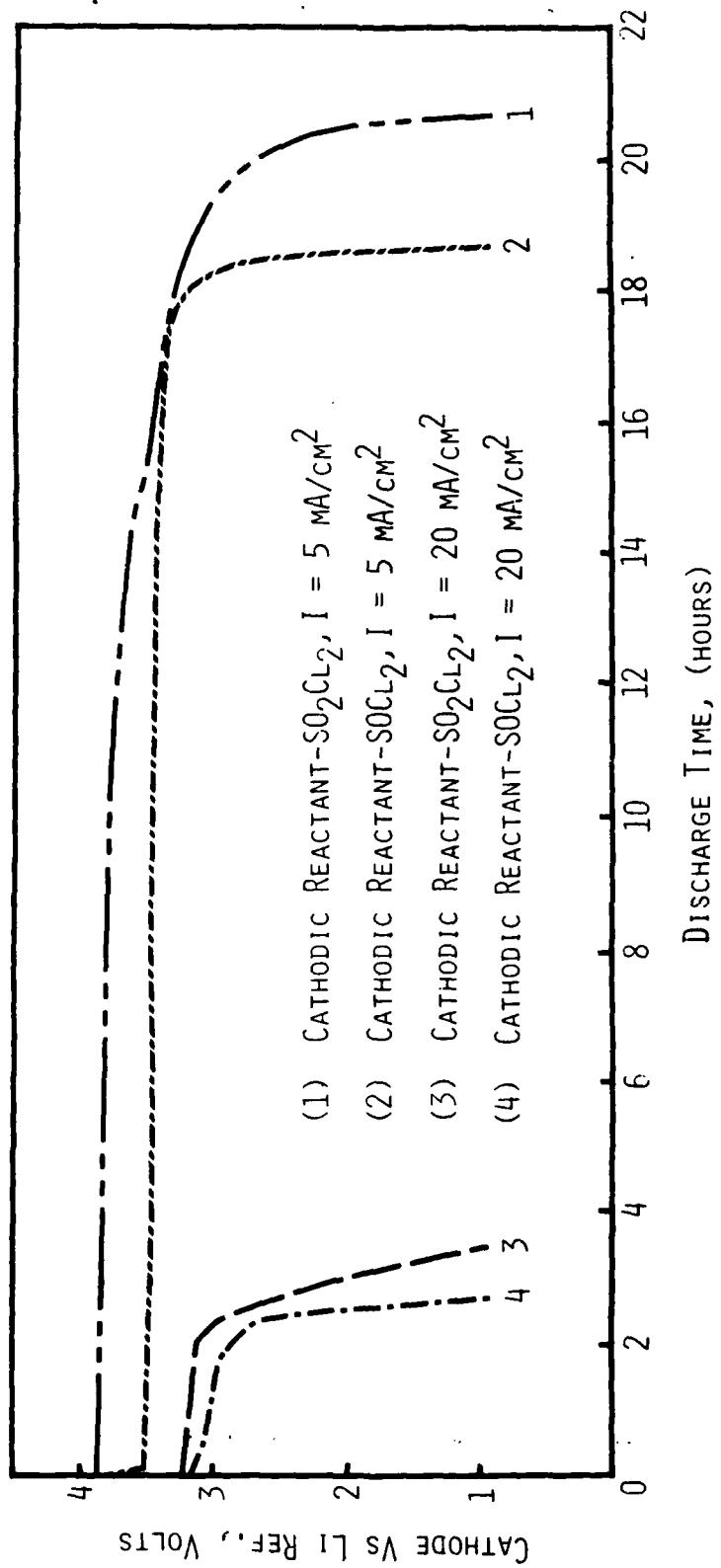


Figure 13. Comparison of Cathodic Discharge Curves for  $\text{SO}_2\text{Cl}_2$  and  $\text{SOCl}_2$